Effect of Hydration and Crystal Form on the Surface Area of Lactose

Abstract

Heating crystalline α-lactose monohydrate at 110 to 130 C, in vacuo, to form anhydrous α-lactose yielded a solid with an expanded surface area as determined by low temperature N_2 or Kr adsorption. The BET area (Brunauer, Emmett, and Teller Equation. J. Amer. Chem. Soc., 60:309. 1938.) of the anhydrous sugar was 2.0 m^2/g while that of the original α-lactose$\cdot H_2O$ was only .18 m^2/g. Rehydration of the anhydrous form to the monohydrate by exposure to H_2O vapor at .72 P_0 at 25 C resulted in only a partial reduction in surface area. Only minor differences were observed among the BET areas of several solid forms of lactose and other sugars of similar sieve size indicating only minor differences in porosity or particle shape which may be related to their potential as sorbents for odorous substances in the atmosphere.

Materials and Methods[1]

Reagent grade α- and β-lactose, dextrose, galactose, maltose, and sucrose were purchased from chemical supply houses. Lactose glass was prepared by spray-drying from an aqueous lactose solution in a 2.7 m Swensen spray dryer in the Dairy Products Laboratory Pilot Plant. S-Lactose, a stable nonhygroscopic form of anhydrous α-lactose originally discovered by Sharp (13), was prepared by heating in a covered container for two hours at 135 C according to Van Kreveld's modification of Sharp's method (15). The polarimetric technique of Sharp and Doob (14) was used to make certain that the S-lactose was really anhydrous α-lactose and that the spray-dried lactose was really the glass and neither the alpha nor beta crystalline form.

Uniform particle size samples of these sugars were prepared for adsorption studies using a ROTAP sieve tester. Samples were se-

lected from powder particles which passed through a 54 μ sieve and were retained on a 44 μ screen.

Introduction

Lactose has been considered especially effective for the adsorption of volatile flavor components and aromas (8, 12) and has therefore been recommended for such diverse industrial applications as air filtration and food flavor enhancement. There is, however, little quantitative data reported on gas or vapor adsorption by lactose or any other sugar.

Nickerson and Dolby (9) recently studied the adsorption of diacetyl by several forms of lactose and other simple sugars and found an inverse relation between diacetyl adsorption and the particle size of the adsorbent. Their studies indicated very little diacetyl absorption by crystalline α-lactose$\cdot H_2O$ and spray-dried lactose glass while conversion of the α-monohydrate to β-lactose or to either of two anhydrous forms of α-lactose resulted in elevated adsorption capacities for diacetyl. Though no surface area data were reported in their paper, Nickerson and Dolby recognized the need to evaluate the importance of such factors as particle size and porosity in affecting vapor adsorption.

Increases in porosity during α-lactose dehydration may explain the reported adsorption properties. Buma (5) stated that desiccation of α-lactose$\cdot H_2O$ leads to drastic changes in crystal structure as he found no difference in the densities of α-lactose$\cdot H_2O$ and anhydrous α-lactose. Herrington (7) concluded from density data that desiccation of α-lactose in vacuo leads to a porous form obtained by loss of water from the crystal lattice without complete rearrangement to form a stable crystal.

The present work was undertaken to determine if there are any differences in the surface areas available for physical adsorption of inert gases among various sugars of uniform particle size and to ascertain to what degree desiccation affects the porosity and surface area of α-lactose. Low temperature (-195 C) gas adsorption, the most widely accepted technique for measuring the surface area of finely divided solids, was chosen for this study.

α-Lactose was also dried by heating under vacuum at 130 C; however, this form of anhydrous α-lactose is very hygroscopic and cannot be exposed to the normal humidity of the laboratory atmosphere, hence no particle size selection is possible with this material.

Nitrogen or krypton adsorption was measured volumetrically in a custom-made glass apparatus of conventional design and operation (1, 10). Nitrogen pressures were measured with a conventional mercury manometer, but krypton pressures were measured with a thermistor gauge (Numinco, Apollo, Pa.), suitable for the low pressures required for Kr adsorption.

Helium (Air Products Co.), used for volumetric calibration, was purified by passage through a charcoal trap at -195 C. The charcoal was previously outgassed at 250 to 300 C for several hours. Ultra-high purity N_2 (Air Products Co.) was passed through a liquid nitrogen cooled trap to remove any condensable vapors. High purity krypton, less than 11.6 ppm impurities, detectable by mass spectrometry, was purchased (Air Reduction Co.) in one liter flasks and sealed into the apparatus and used without further attempts at purification.

Before adsorption measurements, the sugars were outgassed at 10^{-6} torr at ambient temperature for a minimum of 16 hr. The sample temperature during adsorption was monitored with either a N_2 filled vapor pressure thermometer or a thermistor gauge (Numinco, Apollo, Pa.) suitable for cryogenic temperatures. Vapor pressures, P_0, for solid krypton were from the data of Fisher and McMillan (6).

Specific surface areas were calculated from the adsorption data using the Brunauer, Emmett, Teller (BET) multilayer equation (4). Accordingly measurements were made in the range of the adsorption isotherm where the BET equation is most reliable, i.e., for $.05 < P/P_0 < .35$.

To examine the effects of hydration on α-lactose particles, the following experimental sequence was adopted: Krypton adsorption measurements were made on a sample of α-lactose•H_2O in the 44 to 54 μ size range; the lactose was then dehydrated in vacuo in the adsorption cell; adsorption measurements were repeated; the now anhydrous α-lactose was exposed to H_2O vapor at .72 relative pressure to reform the crystalline monohydrate; and finally krypton adsorption measurements were repeated with the same sample, now

TABLE 1. Surface areas of various sugars of uniform particle size.

Sugar	Area
	(m²/g)
Sucrose	.36
Dextrose	.78
Galactose	.25
Maltose	1.18
α-Lactose•H_2O	.18
Lactose glass	.17
S-Lactose	.47
β-Lactose	.64

α-lactose•H_2O once more. These measurements were all in the BET range $.05 < P/P_0 < .35$; however, to investigate porosity changes a larger sample of α-lactose•H_2O was carried through the same experimental sequence except that complete N_2 adsorption-desorption isotherms were measured for the anhydrous and the rehydrated α-lactose.

Results

Surface areas obtained with the uniform particle size samples of the various sugars investigated are presented in Table 1. These are apparently all low area materials with only minimal differences between them. Maltose alone possesses an area slightly larger than the others.

The effects of removing water of crystallization from α-lactose• H_2O are shown with the data in Table 2. Dehydration caused an approximately ten-fold increase in surface area, from .18 to 2.0 to 2.2 m²/g; however, rehydrating the anhydrous α-lactose to reform the crystalline monohydrate resulted in only a small partial loss in surface area. The surface area, 1.2 m²/g, calculated from data for a

TABLE 2. Surface area of α-lactose in different stages of hydration.

Form	Sample[a]	Area
		(m²/g)
α-Lactose•H_2O	1	.18
	2	.18
Anhydrous α-lactose	1	2.19
	2	2.04
α-Lactose•H_2O	1	1.60
	2	1.92
	2[b]	1.19

[a] Samples 1 and 2 each refer to a single lactose sample carried through the dehydration-rehydration sequence.

[b] Sieved portion of rehydrated Sample 2.

sample of uniform size α-lactose·H_2O particles obtained by selecting rehydrated α-lactose particles between the 44 and 54 μ limits clearly shows that the changes in surface area on dehydration cannot be attributed to gross particle size alterations only. Comparison of data in Tables 1 and 2 shows that the nonhygroscopic form of anhydrous α-lactose, S-lactose, has a lower surface area than the hygroscopic form. In all conversions between hydrated and anhydrous α-lactose the mass changes were exactly 5% of the mass of the hydrate or one mole H_2O per mole anhydrous lactose.

Nitrogen adsorption and desorption data for anhydrous α-lactose (Sample 2) are shown graphically as the isothermal curve in Figure 1; and similarly N_2 adsorption and desorption isotherms obtained after rehydration of the same sample are in Figure 2. In each case, limited hysteresis was observed at $P/P_0 \geq .8$, but at all lower relative pressure values the adsorption and desorption curves were identical.

Discussion

Surface areas of .18 m²/g and .64 m²/g reported here for α-lactose·H_2O and β-lactose, respectively, are not in disagreement with
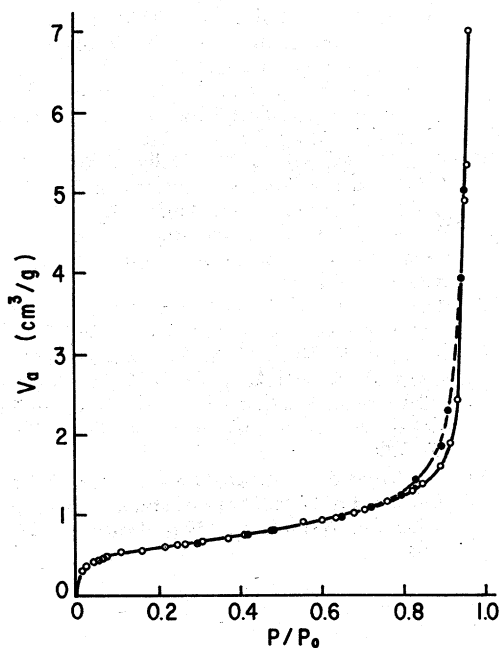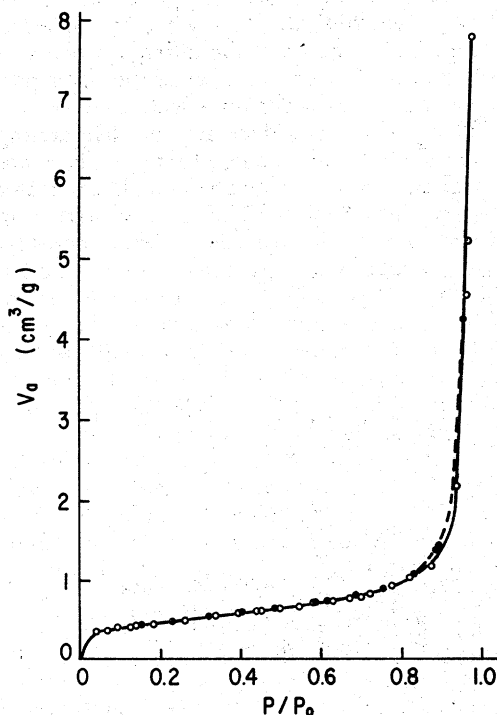

Fig. 2. Nitrogen adsorption and desorption isotherms (−195 C) on rehydrated α-lactose·H_2O.

those of .33 m²/g and .83 m²/g reported earlier (2). The present data were obtained with samples in a selected particle size range, whereas the older data were determined with unsized samples. Furthermore, the present data were calculated from Kr adsorption data which are more accurate than N_2 adsorption data for such low surface area absorbents.

The small differences in surface areas of the various sugars (Table 1) do not represent any major differences in porosity but rather minor irregularities in particle shape. If any of the sugars contain any pore space, it is certainly very limited, and no complex capillarity is present. This can be further demonstrated by computation of a roughness factor which is defined as the ratio of the total surface area (BET) including that of any pore walls to a smooth outer surface only area. A surface area for spherical particles may be calculated from the equation: $d = 6/\rho\delta$, where d is the particle diameter, ρ is the density, and δ is the specific surface area (10). Using our published densities of α- and β-lactose (3) and assuming, as a first approximation, that the sugar particles are spheres of 50 μ diameter, roughness factors of 2.3 and 8.4 were obtained

Fig. 1. Nitrogen adsorption and desorption isotherms (−195 C) on anhydrous α-lactose.

for the crystalline α- and β-lactose. Neither of these values indicates highly porous materials and probably represent the difference between spheres and the actual shapes of the sugar particles, e.g., tomahawks for α-lactose $\cdot$ H_2O.

The increase in surface area on dehydrating α-lactose $\cdot$ H_2O in vacuo, Table 2, is more significant with a calculated roughness factor for the anhydrous form of 27.1, representing either changes in particle size or porosity. These results are in keeping with the notion (3, 5, 7) that anhydrous α-lactose is an expanded crystal form, however, no large internal pore volume is present as evidenced by the lack of hysteresis in the N_2 desorption isotherm (-195 C) below .8 P_0 (Fig. 1). Computation of pore size distributions from the N_2 adsorption isotherms, using the method of Pierce (11), showed that the entire pore volume can be accounted for with pores larger than 180 A in diameter for the anhydrous α-lactose and larger than 140 A for the rehydrated α-lactose.

A plausible explanation for these data may be that on heating the hydrate large cracks are formed in the crystalline particles due to the pressure of the escaping water vapor. Such cracks, of course, are not mended on rehydration. Dehydration, therefore, results in increased surface areas but with porosity limited to large pores or the interparticle condensation range of the adsorption isotherm only, and rehydration should not result in reversion to the original small surface area.

Nickerson and Dolby's report (9) of an increase in diacetyl adsorption by lactose after heating to the anhydrous form agrees with our data. Their absorption measurements were made by bubbling air through diacetyl and then passing the air through a sugar column. Though the porosity we detected in anhydrous α-lactose particles involves only wide pores, they are of appropriate dimensions to be significant in gas flow systems as employed by those investigators (9). These wide pores may also be significant in adsorption of aromas or volatile flavor components as it is entirely conceivable that such odorous molecules may be large enough for dimensions of the wider pores to be limiting on adsorption capacity. Further quantitative studies are needed to substantiate claims concerning the unique advantages of lactose for vapor adsorption and to seek out a mechanism to rationalize such phenomena, if they truly exist.

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